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Sixth Quarterly Progress Report

PROCESSING, APPLICATION, AND EVALUATION OF SEALANTS FOR FUEL TANKS IN ADVANCED AEROSPACE STRUCTURES

Contract No. NAS8-21399
DCN-1-8-54-10238 (1F)

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to

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Marshall Space Flight Center, Alabama

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DAYTON, OHIO 45407

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For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
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ABSTRACT

The goal of this program is to develop and evaluate improved thermally resistant sealants for use in fuel tanks of advanced high-speed aircraft. The current effort involved evaluating Dow Corning's 77-028 fluorosilicone, MANE 482 Viton C-10 and Quantum's Q-112 and Q-113.

The Dow fluorosilicone sealant satisfactorily withstood the 500°F air exposure, but was severely degraded by 500°F fuel vapor exposures. The two primers evaluated provided similar levels of sealant adhesion, which appeared adequate. An HF acid pickle did not produce a noticeable increase in sealant adhesion over the MIBK solvent treatment.

The MANE 482 Viton sealant satisfactorily withstood all three 500°F environmental exposures. The combination adhesive-cohesive strengths remained at or near the minimum property requirement values of 500 psi shear strength and 15 ppi peel strength.

The 500°F exposure environments were too severe for the two polyimide sealants, in their present state of development. The sealants reverted to liquid form in all three environments.

Infrared spectrographic analyses were run on the liquid and vapor fuel environments after exposure to the various sealants at 500°F. These indicated that the Viton and fluorosilicone sealant degradation products had induced a fluorination reaction with components of the hydrocarbon fuel. No degradation products from the polyimide sealants were detected in the liquid fuel samples.

After 1000 hours of exposure the fluorosilicone and two polyimide sealants had not induced stress corrosion cracking in any of the bars tested. However, five tensile bars coated with the Viton sealant all failed by stress corrosion within 400 hours, even though the Viton elastomer had been pretreated with piperazine prior to compounding for removal of most corrosion causing HF-amine salt.

Thermal gravimetric analyses showed that the Viton and fluorosilicone sealants have good thermal stability and oxidative resistance. The two polyimide sealants have degradation temperatures that are approximately 150 to 200°F lower than the Viton or fluorosilicone degradation temperatures.

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I. INTRODUCTION

This study is Task B of a three-task program whose overall goal is the development of improved thermally resistant sealant materials for use in fuel tanks of advanced high-speed aircraft. The object of this task is the formulation, application, evaluation, and process engineering of new sealant materials. This phase has initially entailed the study of advanced state-of-the-art materials, and new materials being developed under Task A and elsewhere are being evaluated as they become available.

A part of the evaluation phase of this task is the definition of the susceptibility of the Ti-6Al-4V alloy to stress corrosion by highly fluorinated sealant systems. The principal objective of this study is to determine if fluorinated polymers, regardless of structure, inherently promote stress corrosion in titanium alloys or if the phenomenon is dependent on polymer structure.

The first year's effort indicated that the Dow Corning fluorosilicones and the Air Force Vitons had the best available high temperature sealant characteristics. Stress corrosion studies also demonstrated that partially fluorinated hydrocarbon sealants are capable of causing stress corrosion when the formation of HF is part of the curing mechanism. A non-curable and fully fluorinated hydrocarbon and a fluorosilicone sealant (both with high thermal stabilities) did not cause stress corrosion of Ti-6Al-4V.

The current work is geared toward complete characterization of the best Viton and fluorosilicone type sealants. Additional promising sealants are being evaluated as they become available and further stress corrosion work will be directed toward identifying the sealant degradation products that induce the corrosion of titanium alloys at 500°F.

The compatibility of Dow Corning 77-028 fluorosilicone sealant, MANE 482 Viton C-10 sealant, and Quantum's Q-112 and Q-113 polyimide sealants with the Ti-6Al-4V alloy and Jet A-50 fuel was evaluated during this period, and several physical properties of each sealant were determined.

The lap shear and peel strengths of these sealants bonded to Ti-6Al-4V sheet were defined after 70-hour exposure to several 500°F environments. Primers 77-037 and 77-006 were evaluated in combination with the 77-028 sealant, and two alloy surface treatments, MIBK solvent wash and HF-HCl-H_3PO_4 acid pickle, were compared for effectiveness in promoting sealant adhesion.

II. RESULTS AND DISCUSSION

A. COMPOSITION AND PROCESSING PROCEDURES FOR PROGRAM SEALANTS

Dow Corning 77-028 fluorosilicone sealant, MANE 482 Viton C-10 sealant, and Quantum Q-112 and Q-113 polyimide sealants were evaluated for their compatibility with Ti-6Al-4V alloy and Jet A-50 fuel. They were also characterized by several physical property determinations. The sealant compositions and processing procedures used in preparing the necessary test specimens are described below.

1. Dow Corning 77-028 Fluorosilicone Sealant

This two part sealant has been developed by Dow Corning as an optimized fluorosilicone formulation for greatest thermal stability and fuel resistance. The sealant was prepared by mixing one part curing agent with ten parts of base material. A vacuum was then applied and broken several times prior to sealant application and cure to obtain bubble-free material. The sealant can be cured at room temperature over a period of seven days; however, all sealant prepared for use in this program was given an accelerated temperature cure of one hour at 300°F.

Fluorosilicone sealants generally exhibit poor adhesion to metal substrates, and primers are normally required to achieve adequate adhesive properties. Primers 77-037 and 77-006 both provided much improved adhesion and these were evaluated in various tests with the Ti-6Al-4V alloy. Dow Corning currently recommends primer 77-037 because it requires only a room temperature cure.

2. MANE 482 Viton C-10 Sealant

This Air Force Materials Laboratory sealant contains the following ingredients:

	Parts
Viton C-10 (piperazine treated)	100
CaO	15
FS-1265 Oil (1000 cs)	4
MEK	40
1,6-Hexanedithiol	1

The Viton sealant was received for evaluation in three parts. The first part consisted of the Viton elastomer compounded with the CaO and FS-1265 oil, and the other two parts comprised the MEK solvent and dithiol curing agent.

The Viton elastomer had been treated with 0.6 phr piperazine to produce double bond curing sites and provide for HF elimination prior to the dithiol cure. Only after being thoroughly washed with water to remove the resulting HF-amine salt was the treated elastomer compounded into a sealant.

The sealant parts were mixed in an Atlantic Research Micromixer (Baker Perkins type mixer) and a vacuum was applied during the last several minutes of mixing. The various test specimens were prepared and then the sealant was given the recommended stepwise temperature cure, consisting of 24-hour temperature cycles at 75, 100, 150, 200, 250 and 300°F.

3. Quantum Q-112 and Q-113 Polyimide Sealants

These two sealants are first generation products which represent the current state of the art. They were procured as dimethylformamide (DMF) solutions, containing approximately 75% solids and having syrup-like viscosities. The dissolved sealants were in the precursor polyamic stage, without fillers or a curing agent, and to be converted to a useful elastomer the solvent had to be removed and a cyclization reaction performed.

The necessary sealant test specimens were prepared from the DMF solutions and then heated 40 hours at 60°C to remove most of the DMF solvent. The sealant cyclization reaction was performed by heating 40 hours at 120°C.

The standard lap shear specimen preparation was modified because of the high solvent content of these sealants. The sealant solutions were applied to the bottom panels on the jigs and then heated two hours at 60°C prior to placement of the upper overlap panels. This preheating step resulted in a more workable sealant with higher solids content, and subsequent application of the solvent removal and cyclization heat cycles resulted in nearly bubble-free sealant.

B. SEALANT FUEL EXPOSURE EVALUATION

1. Lap Shear and Peel Panel Testing

The lap shear and peel strengths of the four test sealants bonded to Ti-6Al-4V were defined after exposure to several 500°F environments. Sealant specimens were exposed for 70-hour periods to the 500°F environments of air, Jet A-50 fuel-air, and Jet A-50 fuel-nitrogen. Seventy-hour, 500°F exposure of the Jet A-50 fuel itself to air causes the hydrocarbon fuel to darken considerably. However, the fuel undergoes no significant change in the nitrogen environment.

a. Dow Corning 77-028 Fluorosilicone Sealant

Lap shear and peel strengths were defined using primers 77-037 and 77-006, plus titanium alloy surface treatments of HF acid solution and MIBK solvent. A summary of the parameter combinations evaluated is shown below:

Ti-6Al-4V Surface Parameters			Number of Test Specimens/Evaluation	
Ti-6Al-4V Treatment	Primer No.	Exposure Environment[1]	Lap Shear	Peel Panel
MIBK	77-037	Controls	5	2
MIBK	77-037	Air	5	2
MIBK	77-037	Air-Fuel	5	2
MIBK	77-037	N_2-Fuel	5	2
MIBK	77-006	Controls	5	2
MIBK	77-006	N_2-Fuel	5	2
HF-HCl-H_3PO_4	77-037	Controls	5	2
HF-HCl-H_3PO_4	77-037	N_2-Fuel	5	2

[1]All exposure environments were applied at 500°F for 70 hours.

The post-exposure properties of the Dow Corning 77-028 sealant are shown in Table I. Exposure of the sealant to 500°F in air produced approximately a 50% loss in the adhesive strength between the primer and sealant, as measured by lap shear tests. The 500°F fuel vapor-air environment caused the sealant to revert to a paste-like fluid, with loss of all useful sealant properties. The 500°F fuel vapor-nitrogen environment severely softened the sealant. The sealant still retained a high degree of elasticity but with very low adhesive strength.

The 77-006 primer appeared slightly better than the 77-037 primer in control lap shear specimens. However, the two primers could not be fairly compared for performance in the 500°F fuel

Table I

INFLUENCE OF SEVERAL 500°F ENVIRONMENTS ON THE BOND PROPERTIES OF DOW CORNING 77-028 FLUOROSILICONE SEALANT

Ti-6Al-4V Surface Parameters		Exposure Test Conditions				Lap Shear Strength			Peel Panel Properties			
									Peel Str.			
Primer No.	Ti-6Al-4V Treatment	Vapor Environment	Temp., °F	Time, hr	Pressure, psig(1)	Sealant Thickness, mils	Shear Str., psi	Failure Mode	Max., ppi	Min., ppi	Failure Mode	Comments
77-037	MIBK	Air	77	Controls		8	29*	80% Adh	14.8	9.0	At	Shore "A" hardness - 35
						6	620	Cohesive	16.6	9.4	screen	
						6	190*	40% Adh				
						6	560	50% Adh				
						4	650	10% Adh				*Values not average
							Av 610		15.7	9.2		
77-037	MIBK	Air	500	70	0	5	360	Adhesive	7.8	2.2	80% Adh	Shore "A" hardness - 35
						6	270	Adhesive	6.6	1.4	Adhesive	
						5	330	Adhesive				
						5	250	Adhesive				
						6	250	Adhesive				
							Av 290		7.2	1.8		
77-037	MIBK	Fuel-N_2	500	70	60	10	22	Adhesive	5.2	3.4	Adhesive	Shore "A" hardness - <5
						8	7	Adhesive	5.4	4.6	Adhesive	Sealant spongy, with
						9	31	Adhesive				fuel odor still strong
						6	4	Adhesive				one week after test
						9	35	Adhesive				
							Av 20		5.3	4.0		
77-037	MIBK	Fuel-Air	500	70	60	6	0	Sealant	0.0		Sealant	Sealant reverted to soft
						6	0	liquefied	0.0		liquefied	paste and ran down into
						5	0	during			during	liquid fuel. Test was
						5	0	exposure			exposure	repeated again with
						7	0					same results.
							Av 0		0.0			
77-006	MIBK	Air	77	Controls		7	670	Cohesive	15.0	12.1	Cohesive	Shore "A" hardness - 35
						9	580	Cohesive	16.0	13.9	Cohesive	
						7	760	Cohesive				
						6	570	Cohesive				
						5	780	Cohesive				
							Av 670		15.5	13.0		
77-006	MIBK	Fuel-N_2	515	70	60	7	0	Specimen	$\sim$1.0		Cohesive	Shore "A" hardness - <1
						9	0	failed	$\sim$1.0		Cohesive	Sealant very soft and
						6	0	cohesively				spongy
						6	0	during				
						7	0	exposure				
							Av 0		$\sim$1.0			
77-037	HF etch	Air	77	Controls		12	470	Cohesive	15.5		Cohesive	Shore "A" hardness - 35
						13	590	Cohesive	13.4		Cohesive	
						7	720	Cohesive				
						7	730	Cohesive				
						11	410	Cohesive				
							Av 580		14.5			
77-037	HF etch	Fuel-N_2	500	70	60	11	38	Adhesive	5.5		Adhesive	Shore "A" hardness - <5
						9	37	Adhesive	5.8			Sealant soft and spongy
						11	42	Adhesive				
						13	52	Adhesive				
						10	40	Adhesive				
							Av 42		5.7			

(1)Pressure develops during test due solely to the heating of the closed bomb; environment is estimated to be 70% fuel vapor when Jet A-50 fuel is present.

vapor-nitrogen environment because of the 515°F temperature which accidentally occurred during the 77-006 primer exposure. This slightly higher temperature caused the sealant to degrade to a material with almost no cohesive strength. Additional testing needs to be done, therefore, to define the post-exposure adhesion properties of 77-028 sealant with the 77-006 primer.

The HF acid etch alloy treatment produced slightly higher post-exposure adhesion properties than the MIBK solvent wash. The two surface preparations resulted in nearly equal unexposed adhesion strengths. The HF acid etch treatment is currently being evaluated for effect in the 500°F air-only environment.

The Dow Corning 77-028 sealant is currently being reevaluated in peel panels and lap shear specimens, using the two primers and alloy surface treatments. A repeat exposure of these specimens to the 500°F environments will help define test reproducibility.

b. MANE 482 Viton C-10 Sealant

Lap shear and peel strengths of this sealant bonded directly to Ti-6Al-4V were defined. The alloy surfaces were prepared by treatment with an HF acid solution or MIBK solvent. A summary of the parameter combinations evaluated is shown below:

Ti-6Al-4V Surface Treatment	Exposure Environment[1]	Number of Test Specimens/Evaluation	
		Lap Shear	Peel Panel
MIBK	Controls	5	2
MIBK	Air	5	2
MIBK	Air-Fuel	5	2
MIBK	N_2-Fuel	5	2
HF	Controls	5	
HF	Air-Fuel	5	

[1] All exposure environments were applied at 500°F for 70 hours.

The post-exposure properties of the Viton sealant are shown in Table II. The sealant was not severely affected by any of the exposure environments.

The MANE 482 sealant had good initial lap shear and peel strengths, with values at 880 psi and 75 ppi respectively. These are well above the minimum property requirements of 500 psi and 15 ppi. Exposure of the sealant to 500°F air produced a lowering of the peel strength to about 15 ppi (the minimum requirement) but also caused an increase in lap shear strength to 1080 psi. The latter may have been caused by additional sealant crosslinking. The 500°F nitrogen-fuel environment caused a lowering of both sealant properties to values slightly greater than the minimum requirements (22.8 ppi peel strength and 540 psi lap shear strength), while the air-fuel environment caused a lowering of both sealant properties to values 20% below the minimum requirements (13.3 ppi peel strength and 380 psi lap shear strength).

The HF solution surface treatment did not appear to have a significant effect on sealant lap shear strength. However, most of the lap shear specimens failed cohesively when tensile tested and thus the maximum adhesive strengths were not actually determined. Either the MIBK or the HF solution surface treatment appears to be adequate for this sealant system.

c. Quantum Q-112 and Q-113 Polyimide Sealants

The lap shear specimens were prepared from the Quantum materials with the sealants bonded directly to the Ti-6Al-4V alloy. Peel tests were not run at this time because of a limited supply of the sealant materials. Although the sealants in their present state of development were not expected to withstand the 500°F exposure environments, they were exposed to these environments

Table II

INFLUENCE OF SEVERAL 500°F ENVIRONMENTS ON THE BOND PROPERTIES OF MANE 482 VITON C-10 SEALANT

Ti-6Al-4V Surface Treatment	Exposure Test Conditions: Vapor Environment	Temp., °F	Time, hr	Pressure, psig[1]	Lap Shear Strength: Sealant Thickness, mils	Shear Str., psi	Failure Mode	Peel Panel Properties: Peel Str. Max., ppi	Min., ppi	Failure Mode	Comments
MIBK	Air	77	Controls		6	940	Cohesive	70	50	Adhesive	Sealant has a light tan color;
					6	965	Cohesive	77	50	Adhesive	Shore "A" hardness - 54
					8	900	Cohesive				
					9	810	Cohesive				
					9	700	Cohesive				
						Av 860		74	50		
MIBK	Air	500	70	0	7	1060	Cohesive	15	8.2	Adhesive	Sealant dark brown but still elastic;
					8	1010	95% Coh	15	12	Adhesive	Shore "A" hardness - 54
					5	1150	95% Coh				
					5	1080	70% Coh				
					6	1100	Cohesive				
						Av 1080		15	10		
MIBK	Fuel-N_2	500	70	60	9	560	Cohesive	15	11	Adhesive	Sealant dark brown but still elastic;
					7	560	95% Coh	30	15	Adhesive	Shore "A" hardness - 57
					10	510	95% Coh				
					11	510	95% Coh				
					4	550	Cohesive				
						Av 540		22	13		
MIBK	Fuel-Air	500	70	60	7	370	90% Adh	16	8.4	Adhesive	Sealant dark brown but still elastic;
					8	380	95% Adh	11	9.5	Adhesive	Shore "A" hardness - 63
					9	410	Adhesive				
					10	350	Adhesive				
					11	400	Adhesive				
						Av 380		14	9.0		
HF etch	Air	77	Controls		13	650	Cohesive				Sealant has a tan color
					11	710	Cohesive				
					7	900	Cohesive				
					13	630	Cohesive				
					7	960	Cohesive				
						Av 770					
HF etch	Fuel-Air	500	70	60	9	370	Cohesive				Sealant dark brown but still elastic
					9	460	85% Coh				
					12	380	70% Coh				
					15	350	90% Coh				
					12	370	90% Coh				
						Av 390					

(1) Pressure develops during test due solely to the heating of the closed bomb; environment is estimated to be 70% fuel vapor when Jet A-50 fuel is present.

in order to establish their present properties and possibly learn something about their degradation products. A summary of the parameter combinations evaluated is shown below:

Ti-6Al-4V Surface Treatment	Exposure Environment[1]	Number of Lap Shear Test Specimens/Evaluation Q-112 Sealant	Q-113 Sealant
MIBK	Controls	4	4
MIBK	Air	4	4
MIBK	N_2-Fuel	4	4
MIBK	Air-Fuel	3	-

[1]All exposure environments were applied at 500°F for 70 hours.

The post-exposure properties of the polyimide sealants are shown in Table III.

The 500°F air exposure caused the sealants to briefly liquefy and then deteriorate to hard and brittle materials with very low cohesive strength. The 500°F fuel vapor environments (air and nitrogen) caused both sealants to liquefy, and the sealants remained soft and tacky even after cooling to room temperature.

The two polyimide sealants possess low adhesive strength to Ti-6Al-4V and a primer may be required for later generation sealants. Quantum is continuing development work to find suitable cross-linking agents that will improve thermal stability.

2. Environmental Analyses for Sealant Degradation Products

Infrared spectrographic analyses were run on the Jet A-50 fuel liquid and vapor contained in each bomb after the 500°F sealant exposures. These infrared absorption spectra were then compared to those for the corresponding environment in which no sealant was exposed. Thus the absorption bands associated with sealant

Table III

INFLUENCE OF SEVERAL 500°F ENVIRONMENTS ON THE LAP SHEAR STRENGTH OF QUANTUM POLYIMIDE SEALANTS Q-112 AND Q-113

Ti-6Al-4V Surface Treatment	Exposure Test Conditions: Vapor Environment	Temp., °F	Time, hr	Pressure, psig(1)		Sealant Q-112: Sealant Thickness, mils	Shear Str., psi	Failure Mode	Sealant Q-113: Sealant Thickness, mils	Shear Str., psi	Failure Mode	Comments
MIBK	Air	77	Controls			6	230	Adhesive	4	110	Adhesive	Sealants have a dark amber color;
						7	210	Adhesive	4	85	Adhesive	Shore "A" hardness: Q-112 = 60
						9	150	Adhesive	4	120	Adhesive	Q-113 = 58
						4	190	70% Adh	20	80	Adhesive	
					Av		195			100		
MIBK	Air	500	70	0		20	20	90% Coh	6	55	90% Coh	Sealants are deteriorated, have black color, and are hard and very brittle
						12	20	70% Coh	9	170	90% Coh	
						14	50	90% Coh	10	10	90% Coh	
						10	100	90% Coh	20	85	Cohesive	
					Av		50			80		
MIBK	Fuel-N_2	500	70	60			0	Cohesive		0	Cohesive	Sealants reverted to a liquid during test; they were still soft and tacky after the test
							0	Cohesive		0	Cohesive	
							0	Cohesive		0	Cohesive	
							0	Cohesive		0	Cohesive	
					Av		0			0		
MIBK	Fuel-Air	500	70	60			0	Cohesive				Same as above
							0	Cohesive				
							0	Cohesive				
					Av		0					

(1)Pressure develops during test due solely to the heating of the closed bomb; the environment is estimated to be 70% fuel vapor at 500°F when Jet A-50 fuel is present.

degradation products could be determined. The pertinent data for each sealant system evaluated are discussed below. A complete listing of all the compounds identified in both the control and sealant systems is given in the Appendix.

a. Dow Corning 77-028 Fluorosilicone Sealant

Analyses of the liquid test fuels after sealant exposure in air and nitrogen indicated that a significant amount of fluorocarbons were present. Whether these came directly from the sealant or were the result of unsaturated fuel fluorination has not been determined.

Analyses of the post-exposure fuel vapors revealed no compounds that were not in the control samples.

b. MANE 482 Viton C-10 Sealant

Analyses of the post-exposure liquid fuels produced infrared absorption patterns very similar to those obtained for the fluorosilicone exposed fuels, indicating that a mixture of fluorocarbons was present. The similarity in fluorocarbons from each sealant-fuel system indicates that components in the fuel are probably being fluorinated by each sealant to form the fluorocarbon mixture.

Analyses of the fuel vapors showed that compounds were present that had not been detected in either the control or fluorosilicone exposed vapors. The compounds have not been identified as yet but the same peaks also appear in the vapors from the polyimide exposures. They could very well be caused by some kind of an ester.

c. Quantum Q-112 and Q-113 Polyimide Sealants

Analyses of the Jet A-50 fuels after exposure to Quantum polyimides by infrared produced patterns very similar to those for the control fuels, indicating that no sealant degradation products were absorbed or formed.

Analysis of the fuel vapor from the Q-112 nitrogen exposure also showed only the same ingredients that were present in the control. However, the vapors from the Q-112 air and Q-113 nitrogen exposures contained the same unidentified compounds that were present after exposure to the Viton sealant. As previously mentioned, these could be low molecular weight esters.

C. STRESS CORROSION TESTING

1. Dow Corning 77-028 Fluorosilicone Sealant

Three replicate solution treated and aged Ti-6Al-4V tensile bars under an 82.5 kpsi applied stress (0.75 σ_{ys}) have been exposed to the fluorosilicone sealant for 1000 hours at temperatures above 500°F, without failure occurring. Post-exposure tensile tests of these specimens at room temperature revealed no signs of corrosion, either visually or from reduced physical properties.

A fourth tensile bar was exposed to the same environment and conditions as above after being pickled in HF-HCl-H_3PO_4 solution and then liberally coated with 77-037 primer. Again, no failure occurred after 1000 hours of testing.

Results from the above tests are listed in Table IV. They indicate that the sealant degradation products will not produce a stress corrosion problem with Ti-6Al-4V. The HF acid pickle prior

Table IV

STRESS CORROSION SUSCEPTIBILITY OF Ti-6Al-4V EXPOSED TO HIGH TEMPERATURE SEALANTS

Applied Stress = 82.5 kpsi

Sealant	Sealant Type	Test Temperature, °F Max.(1)	Test Temperature, °F Equilibrium(2)	Failure Time, hr(3)	Comments
DC 77-028	Fluorosilicone	750	600	1000 N.F.	Sealant friable and deteriorated
		550	530	1000 N.F.	Sealant soft and bubbly
		530	510	1000 N.F.	Sealant soft and bubbly
DC 77-037(4)	Primer	530	510	1000 N.F.	Sealant soft and bubbly
MRC Viton C-10, amine	Fluorocarbon	750	600	53	Sealant softened but still elastic
		750	600	20	
		600	500	516	
MANE 482, dithiol cured	Fluorocarbon	750	600	25	Sealant changed from tan to dark brown color but still elastic
		680	530	140	
		550	530	385	
		510	500±5	190	
		505	500±5	378	
Q-112	Polyimide	560	500	1000 N.F.	Sealants flowed initially and then became hard and brittle
Q-113	Polyimide	680	500	1000 N.F.	Same as above

(1) Maximum overshoot temperature reached during furnace heat-up.
(2) Equilibrium furnace temperature for balance of test.
(3) N.F. = No failure occurred within the time specified, alloy retained 100% of original tensile and yield strengths.
(4) Ti-6Al-4V tensile bar was etched in HF-HCl-H_3PO_4 solution and then coated with 77-037 primer, prior to 77-028 sealant application.

to primer application also does not appear likely to induce stress corrosion cracking in the Ti-6Al-4V.

2. MANE 482 Viton C-10 Sealant

Five replicate Ti-6Al-4V tensile bars under 82.5 kpsi applied stress and coated with Viton sealant have failed within 400 hours of testing time at temperatures above 500°F. Each bar underwent a considerable amount of corrosion across the failure cross-sectional area as pictorially shown in Figure 1. Actual test times and temperatures are shown in Table IV. These are compared with values for the previously evaluated MRC Viton C-10 sealant (amine cured) which also caused corrosion after only a short exposure time.

The results show that this Viton sealant formulation will cause Ti-6Al-4V stress corrosion cracking at temperatures of 500°F or greater, even though the elastomer had been pretreated for removal of most corrosion causing HF-amine salts. The rate of corrosion appears to be directly proportional to the test temperature.

3. Quantum Polyimide Sealants Q-112 and Q-113

Single Ti-6Al-4V tensile bars coated with the Quantum polyimide sealants have withstood 1000 hours of stress corrosion testing at 500°F without a failure occurring (Table IV). Post-exposure tensile tests of these specimens at room temperature revealed no signs of corrosion, either visually or from reduced physical properties.

The two polyimide sealants do not contain crosslinking agents at this stage of their development. Additional stress corrosion studies should be undertaken once these are incorporated into the sealants.

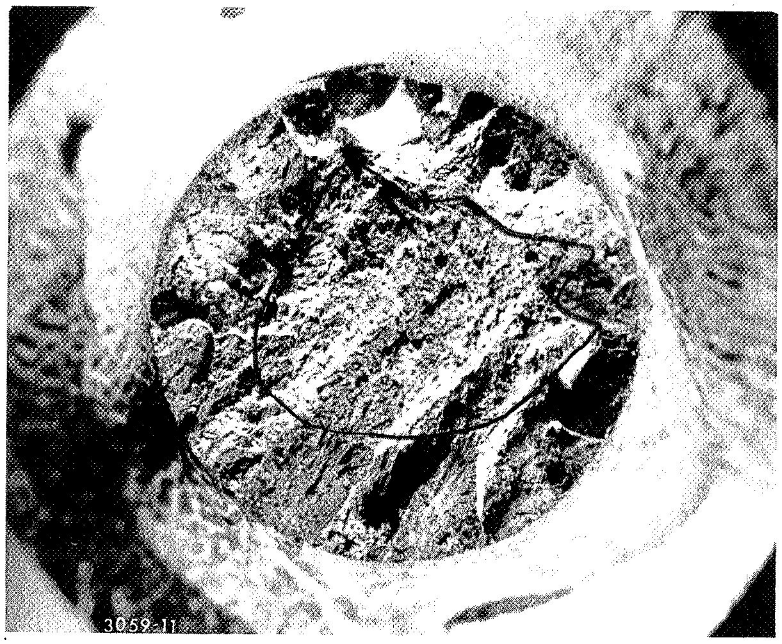


Fig. 1 - Cross Section of MANE 482 Viton Coated Ti-6Al-4V Tensile Specimen that Failed at 530°F Under a Stress of 0.75 σ_{ys} (82.5 kpsi). The Dark Areas Around the Circumference of the Specimen are Stress Corrosion Cracks. (Magnification 10X)

D. SEALANT PHYSICAL PROPERTY DETERMINATIONS

1. Durometer "A" Hardness

The Shore "A" hardness of the test sealants was measured immediately after preparation and again after the 500°F environmental exposures. Below is a table summarizing the representative values obtained with each of the four sealants evaluated.

Table V

SHORE "A" HARDNESS OF SEALANTS AFTER EXPOSURE TO 500°F ENVIRONMENTS

Sealant	Shore "A" Hardness			
		After 70 Hours at 500°F in		
	Initial Hardness	Air	N_2-Fuel Vapor	Air-Fuel Vapor
DC 77-028	35	35	17	0
MANE 482	54	54	57	63
Q-112	58	--	0	0
Q-113	60	--	0	0

The results show that when sealant degradation begins the 77-028 fluorosilicone tends to soften while the 482 Viton tends to stiffen slightly. Both Quantum sealants liquefied when exposed to fuel vapor at 500°F.

2. Sealant Swell and Weight Loss

Sealant swell and weight change after 500°F fuel vapor exposures were determined for DC 77-028 and MANE 482 sealants. The procedure followed was basically that of Method 6211 of Federal Test Method No. 601. However, the sealants were not rinsed in solvent, prior to or after fuel vapor exposure.

Two MANE Viton and one DC fluorosilicone specimens were individually exposed 70 hours to fuel vapor and nitrogen at 500°F. Single specimens of each sealant were also similarly exposed to fuel vapor and air. The sealant specimens were weighed immediately before and after exposure, both in air and water, and the weight and volume changes were then calculated. The results are shown in the following table.

Table VI

SEALANT WEIGHT CHANGE AND SWELL
AFTER 500°F JET A-50 FUEL VAPOR EXPOSURES FOR 70 HOURS

Sealant:	MANE 482 Viton C-10		DC 77-028 Fluorosilicone	
500°F Exposure Environment:	N_2-Fuel	Air-Fuel	N_2-Fuel	Air-Fuel
Environmental Pressure, psig:	60	60	60	60
% Weight Change:	+3.69	+4.43	1.51	Sealant Liquefied
% Volume Change (Swell):	+8.65	+8.60	0.00	

The Viton sealant swelled considerably more than the fluorosilicone but the magnitude is probably not large enough to be of serious concern.

3. Tensile Strength and Ultimate Elongation

Tensile strength studies before and after 500°F environmental exposures were performed with DC 77-028 and MANE 482 sealants. Tensile specimens (Die "C", ASTM D412) were cut from cast sealant sheets approximately 1/16 inch thick. The test results are shown in Table VII.

Table VII

INFLUENCE OF SEVERAL 500°F ENVIRONMENTS ON THE TENSILE STRENGTHS OF DC 77-028 AND MANE 482 SEALANTS

Sealant	Exposure Test Conditions: Vapor Environment	Temp., °F	Time, hr	Pressure, psig(1)		Ultimate Tensile Strength, psi		Elongation, %	Comments
77-028	Air	77	Controls			540		270	Shore "A" hardness - 37
						850		310	
						720		280	
						530		230	
						700		270	
					Av	670		270	
77-028	Air	500	70	0		330		140	Shore "A" hardness - 37
						420		160	Specimens tore at grip ends
						320		130	during exposure, from own weight
						380		160	
					Av	360		150	
77-028	N_2(2)-Fuel	500	70	60		---		---	Four sealant specimens tore from rack during exposure and flowed into the liquid fuel
MANE 482	Air	77	Controls			320	(35)(3)	280	Shore "A" hardness - 58
						290	(40)	370	Specimens contained bubbles at
						460	(10)	430	failure cross-sectional area
					Av	360		360	
MANE 482	Air-Fuel	500	70	60		420	(45)	180	Shore "A" hardness - 58
						460	(30)	190	Specimens contained bubbles at
						520	(20)	260	failure cross-sectional area
					Av	470		210	

(1) Pressure develops during test due solely to the heating of the closed bomb; environment is estimated to be 70% fuel vapor when Jet A-50 fuel is present.
(2) The environment contained about 0.8 vol. % O_2 instead of the normal 0.04 vol. %.
(3) The figures in parentheses are the estimated percent void areas at the failure cross section.

The 70-hour 500°F air exposure caused about a 50% lowering in the 77-028 sealant tensile strength and elongation. The sealant became soft enough during the fuel vapor-nitrogen exposure to tear from the specimen holders and fall into the liquid fuel. Thus, the tensile strength could not be determined. It is estimated to be quite low, however. It should be noted that this particular exposure environment contained approximately 0.8 volume percent oxygen instead of the usual 0.04 volume percent oxygen.

The MANE 482 tensile specimens contained a considerable number of bubbles at the fracture cross section. The estimated void areas are listed in Table VII. Thus, the tensile values reported in the table are all considerably lower than the true values. This Viton sealant is reported by the Air Force to have a tensile strength of 885 psi and a corresponding elongation of 735%, compared to the 360 psi strength and 360% elongation obtained on these samples.

The fuel vapor-air exposure caused the Viton sealant to harden, resulting in a significant increase in tensile strength and a loss of elongation.

4. Thermal Gravimetric Analyses (TGA)

Thermal gravimetric analyses were made on MANE 482, Q-112, and Q-113 sealants in helium and air environments, with a gas flow rate of 0.04 cubic foot per hour. The TGA curves are shown in Figures 2 through 7. The TGA curves for the MRC Viton and DC 77-028 sealants were shown in the previous quarterly report. A comprehensive summary of TGA results for all the sealants tested to date is given in Table VIII.

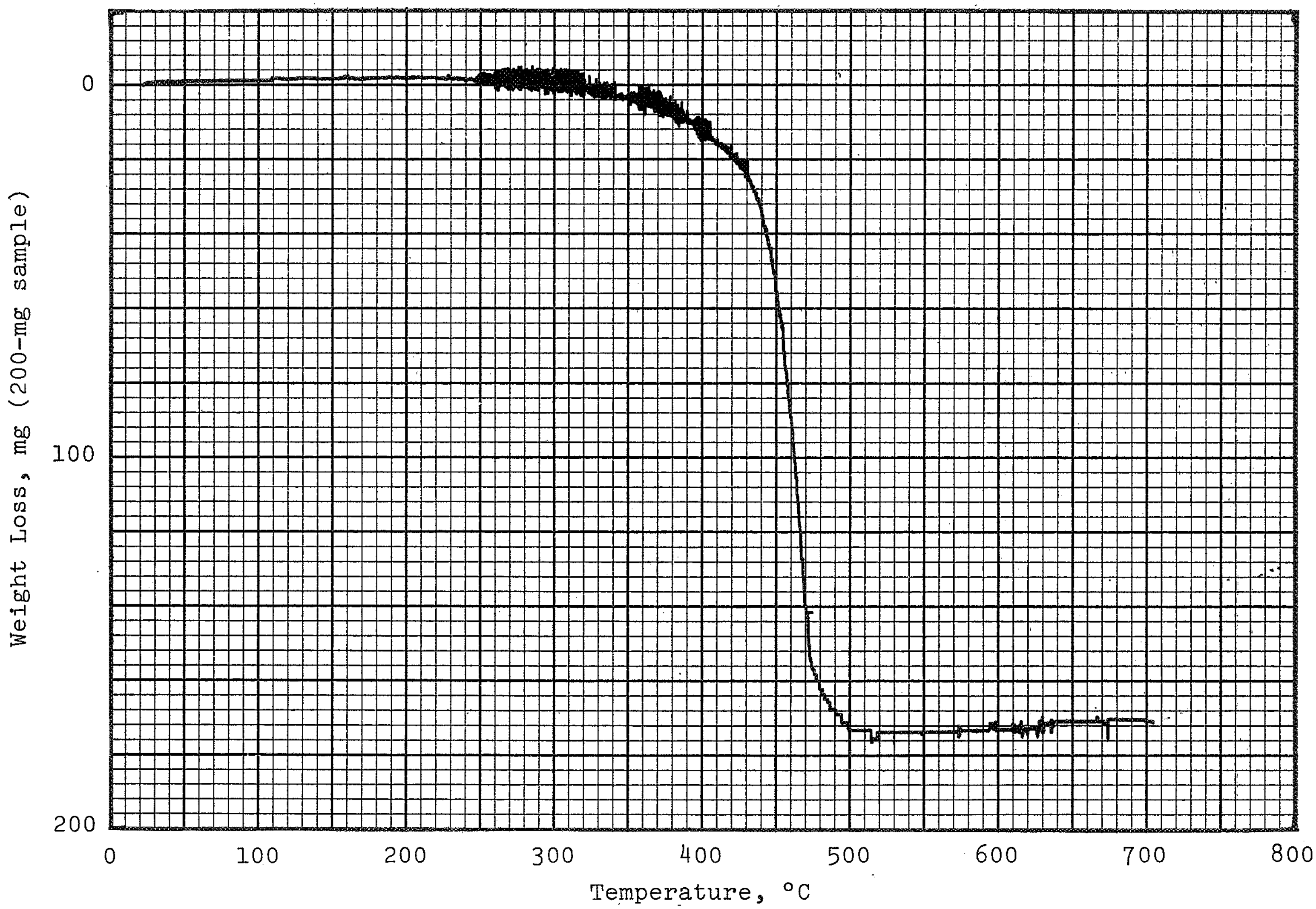


Fig. 2 - Thermal Gravimetric Analysis of MANE 482 Viton C-10 Sealant in Air (0.04 ft^3/hr Gas Flow) at a 2.6°C/min Heating Rate

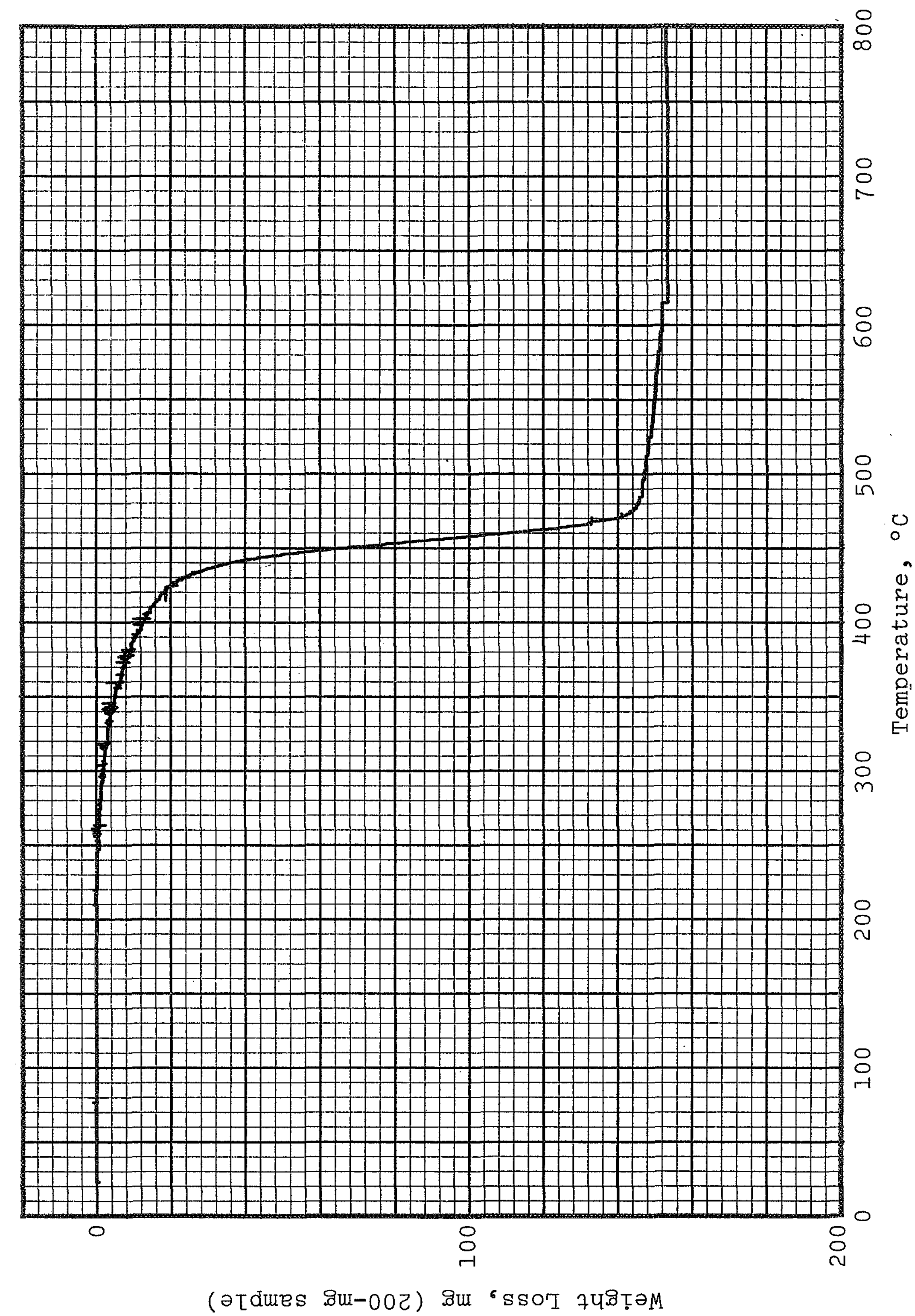


Fig. 3 - Thermal Gravimetric Analysis of MANE 482 Viton C-10 Sealant in Helium (0.04 ft^3/hr Gas Flow) at a 2.7°C/min Heating Rate

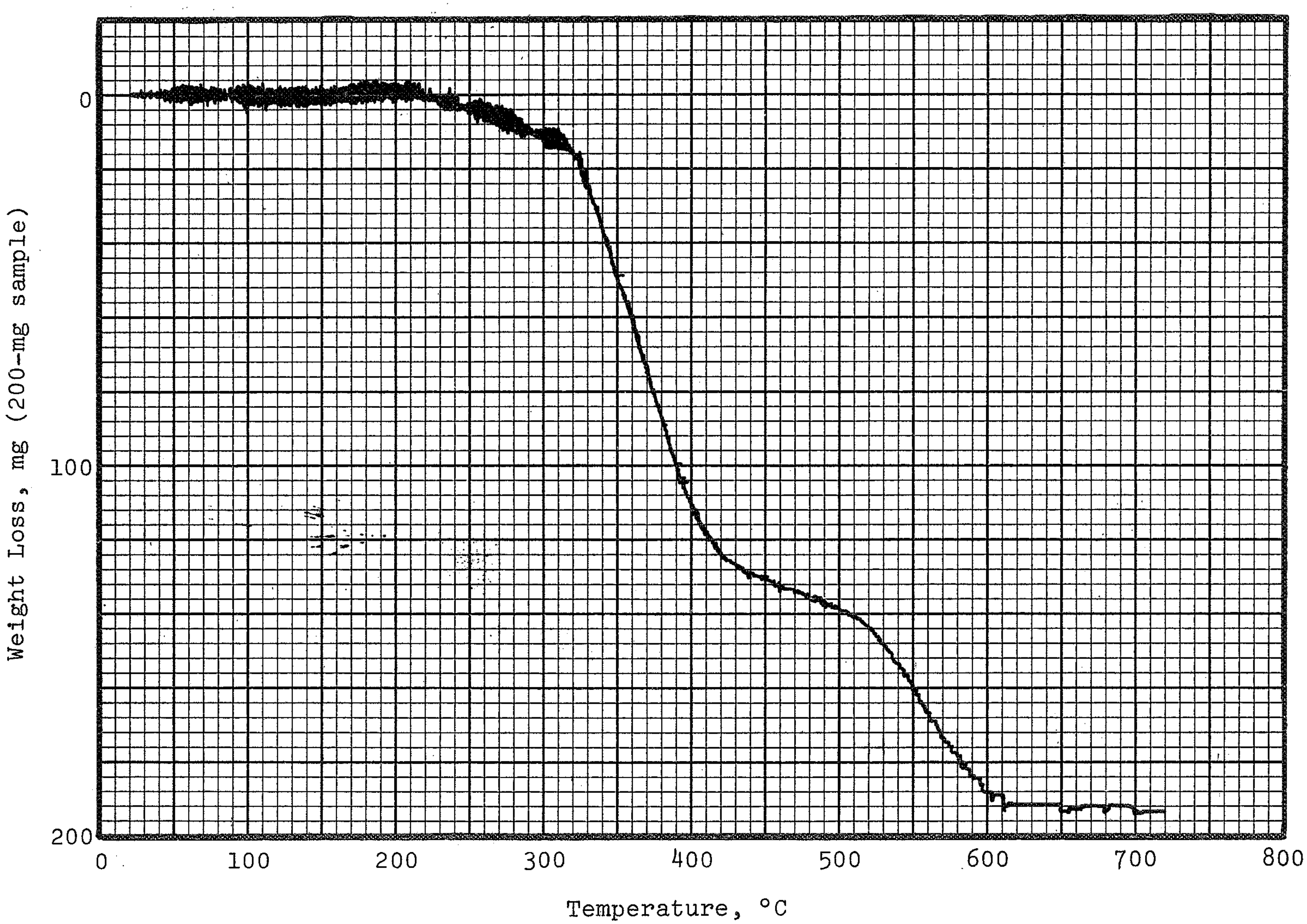


Fig. 4 - Thermal Gravimetric Analysis of Quantum Polyimide Sealant Q-112 in Air (0.04 ft^3/hr Gas Flow) at a 2.6°C/min Heating Rate

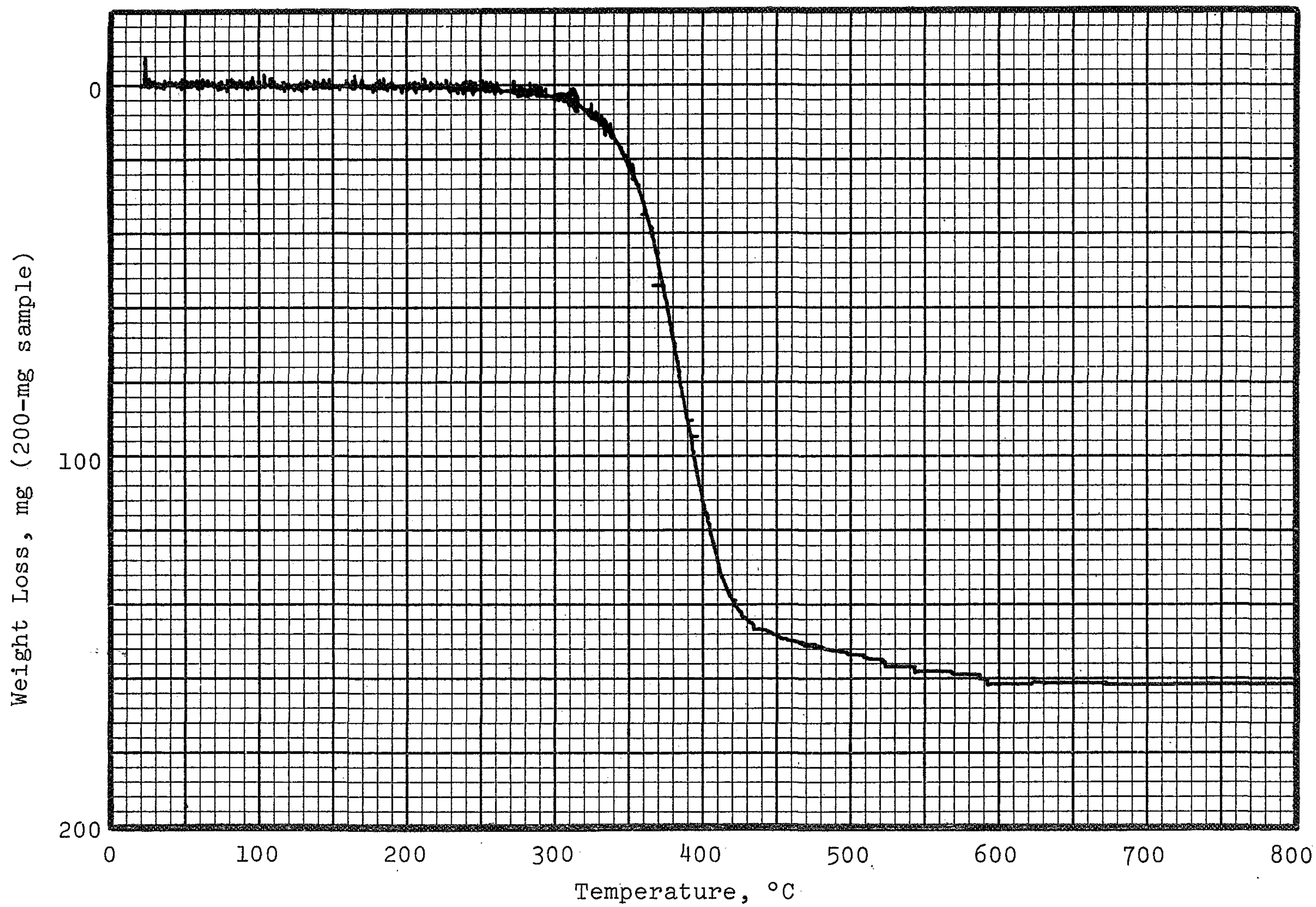


Fig. 5 - Thermal Gravimetric Analysis of Quantum Polyimide Sealant Q-112 in Helium (0.04 ft^3/hr Gas Flow) at a 2.7°C/min Heating Rate

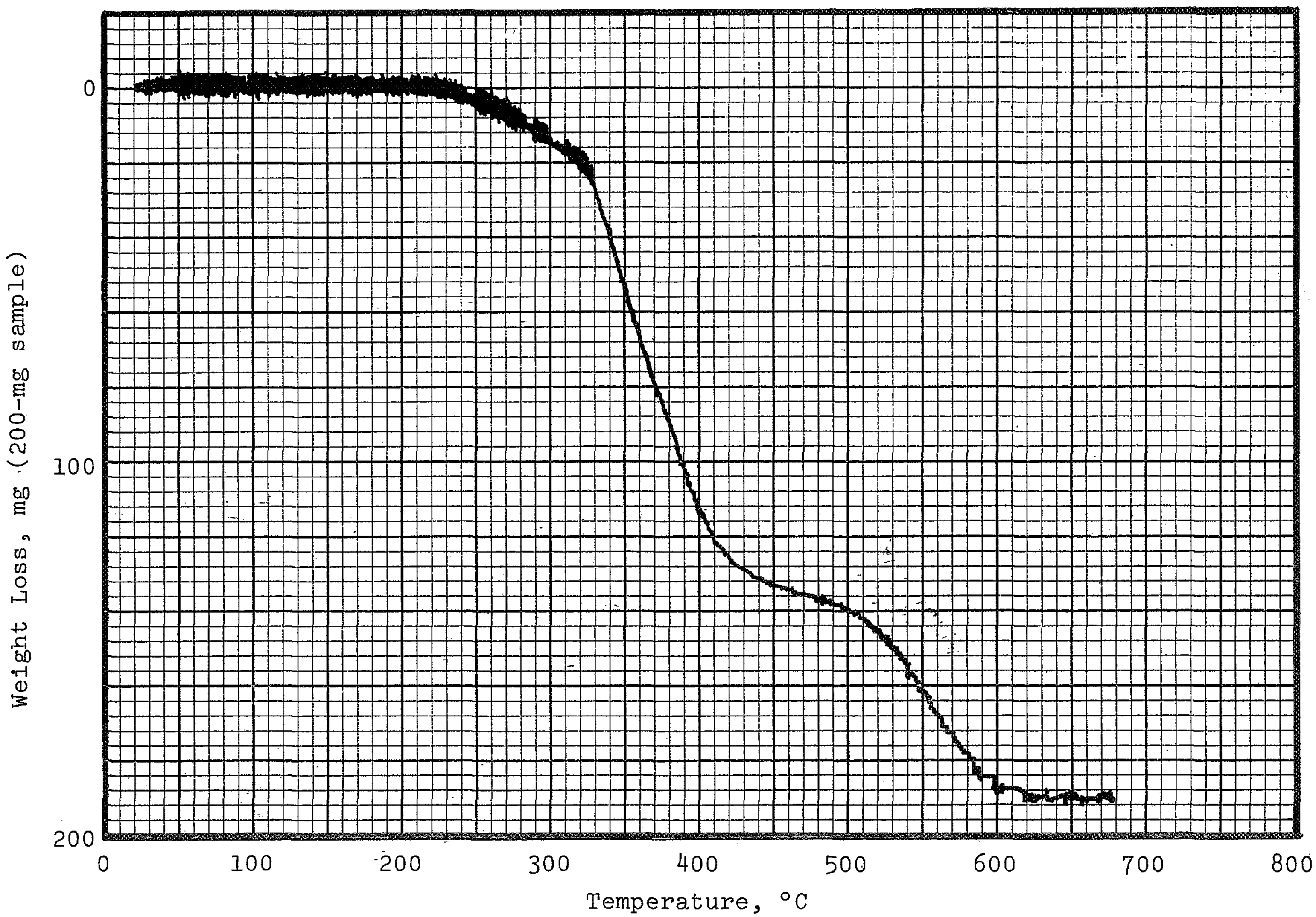


Fig. 6 - Thermal Gravimetric Analysis of Quantum Polyimide Sealant Q-113 in Air (0.04 ft^3/hr Gas Flow) at a 2.6°C/min Heating Rate

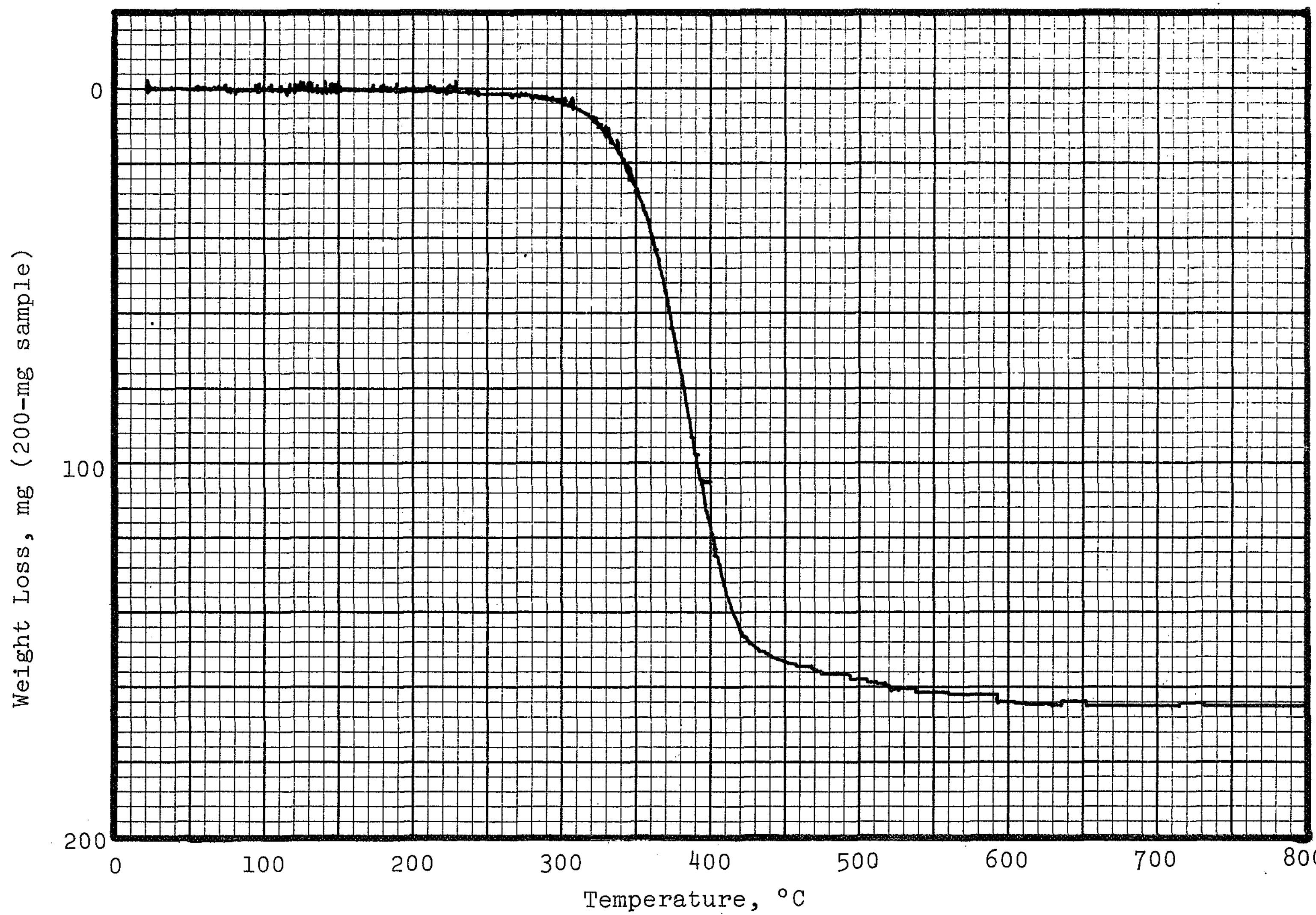


Fig. 7 - Thermal Gravimetric Analysis of Quantum Polyimide Sealant Q-113 in Helium (0.04 ft^3/hr Gas Flow) at a 2.7°C/min Heating Rate

Table VIII

SUMMARY OF SEALANT THERMAL GRAVIMETRIC ANALYSIS RESULTS

Sealant	Analysis Environment	Temperature, °F(°C), at which Sealant Lost: 5% of Weight	10% of Weight	50% of Weight	% Sealant Weight Lost at 1472°F (800°C)
MRC Viton C-10	Air	735(390)	790(420)	860(460)	94
	Helium	700(370)	790(420)	860(460)	74
MANE 482 Viton C-10	Air	735(390)	790(420)	860(460)	85
	Helium	725(385)	795(425)	860(460)	76
DC 77-028 Fluorosilicone	Air	715(380)	750(400)	805(430)	76
	Helium	805(430)	870(465)	940(505)	78
Quantum Q-112 Polyimide	Air	555(290)	615(325)	735(390)	97
	Helium	625(330)	660(350)	745(395)	81
Quantum Q-113 Polyimide	Air	535(280)	610(320)	735(390)	95
	Helium	615(325)	645(340)	735(390)	83

The MANE 482 Viton sealant exhibited good thermal stability and oxidative resistance, very similar to the previously evaluated MRC Viton sealant.

The two polyimide sealants exhibited almost identical thermal degradation characteristics. However, the temperatures at which they lost 5 and 10 percents of their weights were 150-200°F lower than corresponding temperatures for the Viton and fluorosilicone sealants.

5. Clash-Berg Transition Temperature Analyses

Clash-Berg analyses were run on all four sealants. The apparent shear modulus values as a function of temperature are graphically shown in Figures 8 and 9. The transition temperatures, T_F, for each sealant are shown in Table IX.

Table IX

CLASH-BERG SEALANT TRANSITION TEMPERATURES, T_F

Sealant	T_F Temperature, °C[1]
DC 77-028 Fluorosilicone	-65
MANE 482 Viton C-10	-15
Q-112 Polyimide	-40
Q-113 Polyimide	-40

[1] The T_F temperature is defined as the temperature at which the apparent shear modulus is equal to 45,000 psi.

These data indicate that the Dow Corning fluorosilicone possesses the best low temperature elasticity of the sealants evaluated. However, the polyimides should perform equally well in advanced aircraft applications and the Viton may provide enough elasticity at -50°F for advanced aircraft applications.

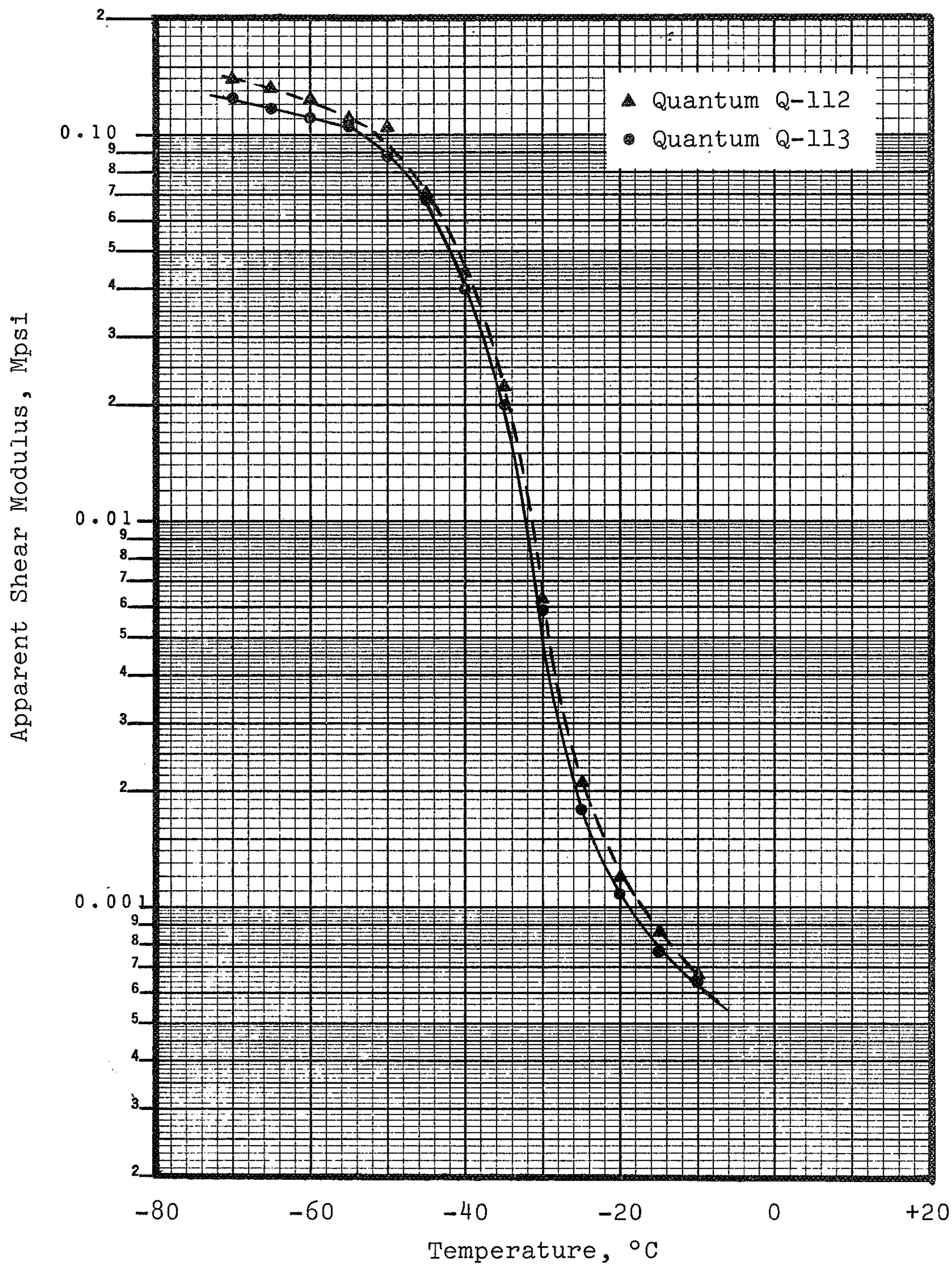


Fig. 8 - Clash-Berg Apparent Shear Modulus vs. Temperature Curves for Quantum Polyimide Sealants Q-112 and Q-113

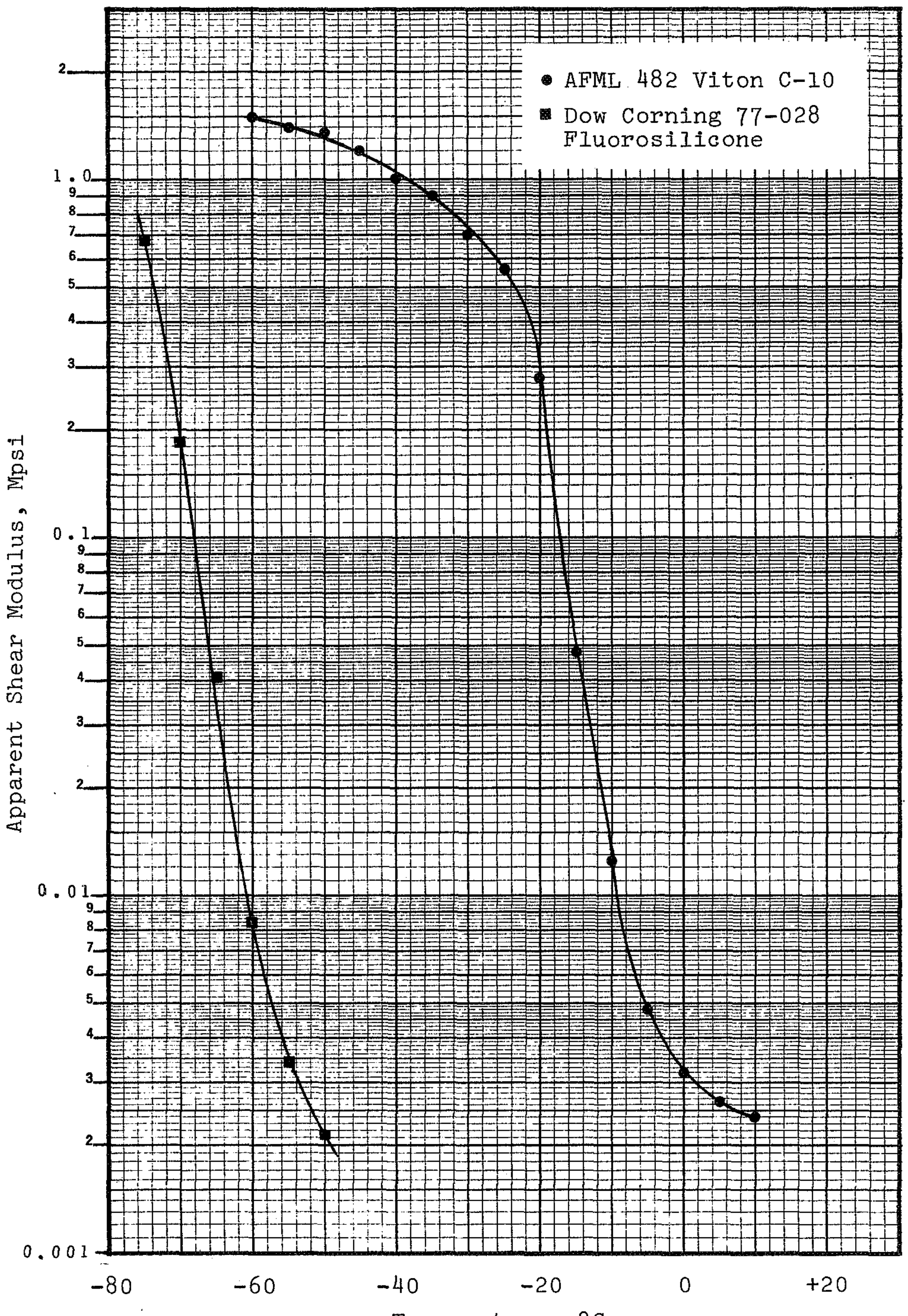


Fig. 9 - Clash-Berg Apparent Shear Modulus vs. Temperature Curves for MANE 482 Viton C-10 Sealant and Dow Corning 77-028 Fluorosilicone Sealant

III. CONCLUSIONS

The Dow Corning 77-028 fluorosilicone sealant has good thermal stability and oxidative resistance at 500°F. Primers 77-037 and 77-006 provide adequate adhesion to Ti-6Al-4V alloy. Initial peel and lap shear strengths with these primers are only slightly greater than the minimum property requirement values of 15 ppi (peel) and 500 psi (shear). A 70-hour exposure to 500°F air produces corresponding values which are only equal to 50% of the minimum property requirements. A 70-hour, 500°F Jet A-50 fuel vapor exposure causes the sealant to severely soften in a nitrogen purged and pressurized system, and to completely liquefy in an air purged and pressurized system. The sealant was found to remain elastomeric at temperatures below -50°F, and its degradation products did not induce stress corrosion cracking of solution treated and aged Ti-6Al-4V alloy within 1000 hours of testing at 0.75 σ_{ys} and 500°F.

The MANE 482 Viton C-10 sealant also has good thermal stability and oxidative resistance at 500°F. The sealant adheres well to Ti-6Al-4V alloy without the use of a primer. Initial peel and lap shear strengths were at least twice as great as the corresponding minimum requirement values. The lap shear and peel strength values remained at or near the minimum requirement values after each of the three 500°F environmental exposures. The sealant tends to harden after aging in 500°F air or fuel vapor, with a corresponding loss in percent elongation. The sealant probably does not retain good elastomeric properties at temperatures near -50°F. The sealant causes Ti-6Al-4V stress corrosion cracking under the conditions described above, at a rate sufficiently high to be of concern.

The Quantum polyimide sealants Q-112 and Q-113 are not sufficiently developed to be useful sealants at 500°F. Both sealants become liquids at these temperatures. Initial lap shear and peel strengths are considerably less than the minimum requirement values and a primer may be required for later generation sealants. The sealants appear to have satisfactory elastomeric properties at -50°F. The sealant degradation products do not cause stress corrosion cracking of the Ti-6Al-4V alloy at 500°F, under the test conditions.

IV. ANTICIPATED WORK

1. Continue literature survey.

2. Retest Dow Corning 77-028 sealant in lap shear and peel panels, with primers 77-037 and 77-006 and alloy surface treatments of MIBK and HF-HCl-H_3PO_4.

3. Evaluate the 77-028 sealant at 450°F in lap shear and peel panels with primer 77-037.

4. Determine the influence of pressure during 500°F exposure of sealants.

5. Identify sealant degradation products in air over a temperature range of 300-700°F, using gas chromatograph and mass spectrometer analyses.

6. Identify fluorinated hydrocarbons believed formed in Jet A-50 fuel during 500°F exposure to the Viton and fluorosilicone sealants.

7. Run Clash-Berg analyses on sealants exposed to the various 500°F environments.

8. Examine tested lap shear and peel panels under the Scanning Electron Microscope, to determine the bonding characteristics of the sealant-primer-alloy interfaces.

9. Initiate stress corrosion testing of second Q-112 and Q-113 sealant specimens; initiate testing of a second DC 77-028 sealant specimen with 77-037 primer.

10. Initiate characterization tests of further developed Quantum polyimides and other new candidate sealants as they become available.

APPENDIX

ENVIRONMENTAL ANALYSES FOR SEALANT DEGRADATION PRODUCTS

Infrared spectrographic analyses were run on the Jet A-50 fuel liquid and vapor contained in the bombs after each 500°F sealant exposure. The infrared absorption spectra were then compared to those for the corresponding environment in which no sealant was exposed, for the purpose of identifying sealant degradation products. The names or types of compounds in each environment that could be identified are given below.

A. ANALYSES OF CONTROL ENVIRONMENTS (NO SEALANT PRESENT) AFTER 70 HOURS AT 500°F

1. Fuel Liquid (Air Exposure):

Contained a mixture of saturated and unsaturated hydrocarbons.

2. Fuel Liquid (Nitrogen Exposure):

Contained a mixture of saturated and unsaturated hydrocarbons, similar to the air-fuel liquid.

3. Fuel Vapor (Air Exposure):

Contained a mixture of saturated and unsaturated hydrocarbons, including methane, ethylene, and benzene. Small amounts of either an ester, acid, or ketone (not acetone) were detected. Large amounts ($\sim$10%) of CO and CO_2 were present, but no H_2O was detected.

4. Fuel Vapor (Nitrogen Exposure):

Contained the same compounds found in the fuel-air vapor sample. However, there were only very small amounts of CO and CO_2 detected.

B. ANALYSES OF ENVIRONMENTS AFTER EXPOSURE TO DOW CORNING 77-028 FLUOROSILICONE SEALANT

1. Fuel Liquid (Air Exposure):

Contained the same compounds that were found in the control, plus a considerable amount of what appears to be a mixture of hydrocarbons of C_3 or greater chain length.

2. Fuel Liquid (Nitrogen Exposure):

Contained the same compounds as described above.

3. Fuel Vapor (Air Exposure):

Contained the same compounds that were found in the corresponding control sample. However, there was a much larger amount of methane present.

4. Fuel Vapor (Nitrogen Exposure):

Contained the same compounds that were found in the control.

C. ANALYSES OF ENVIRONMENTS AFTER EXPOSURE TO MANE 482 VITON C-10 SEALANT

1. Fuel Liquid (Air Exposure):

Contained the same ingredients that were found in the corresponding 77-028 sealant sample, with a mixture of fluorocarbons suspected of being present.

2. Fuel Liquid (Nitrogen Exposure):

Contained the same compounds as described above.

3. Fuel Vapor (Air Exposure):

Contained the same ingredients found in the control, plus some unidentified components having absorption bands at 7.90, 8.45, and 8.65 micron wavelengths. These were not detected in the fluorosilicone sealant samples but were found in the vapors exposed to the polyimide sealants. Water was also detected, but only a fraction of the CO_2 found in the control test was present.

4. Fuel Vapor (Nitrogen Exposure):

Contained the same ingredients as described above, but no water vapor.

D. ANALYSES OF ENVIRONMENTS AFTER EXPOSURE TO QUANTUM Q-112 AND Q-113 POLYIMIDE SEALANTS

1. Fuel Liquid (Air Exposure, Q-112 Sealant):

Contained only the same ingredients as found in the control liquid.

2. Fuel Liquids (Nitrogen Exposure):

Both contained only the same ingredients as found in the control liquid.

3. Fuel Vapor (Air Exposure, Q-112 Sealant):

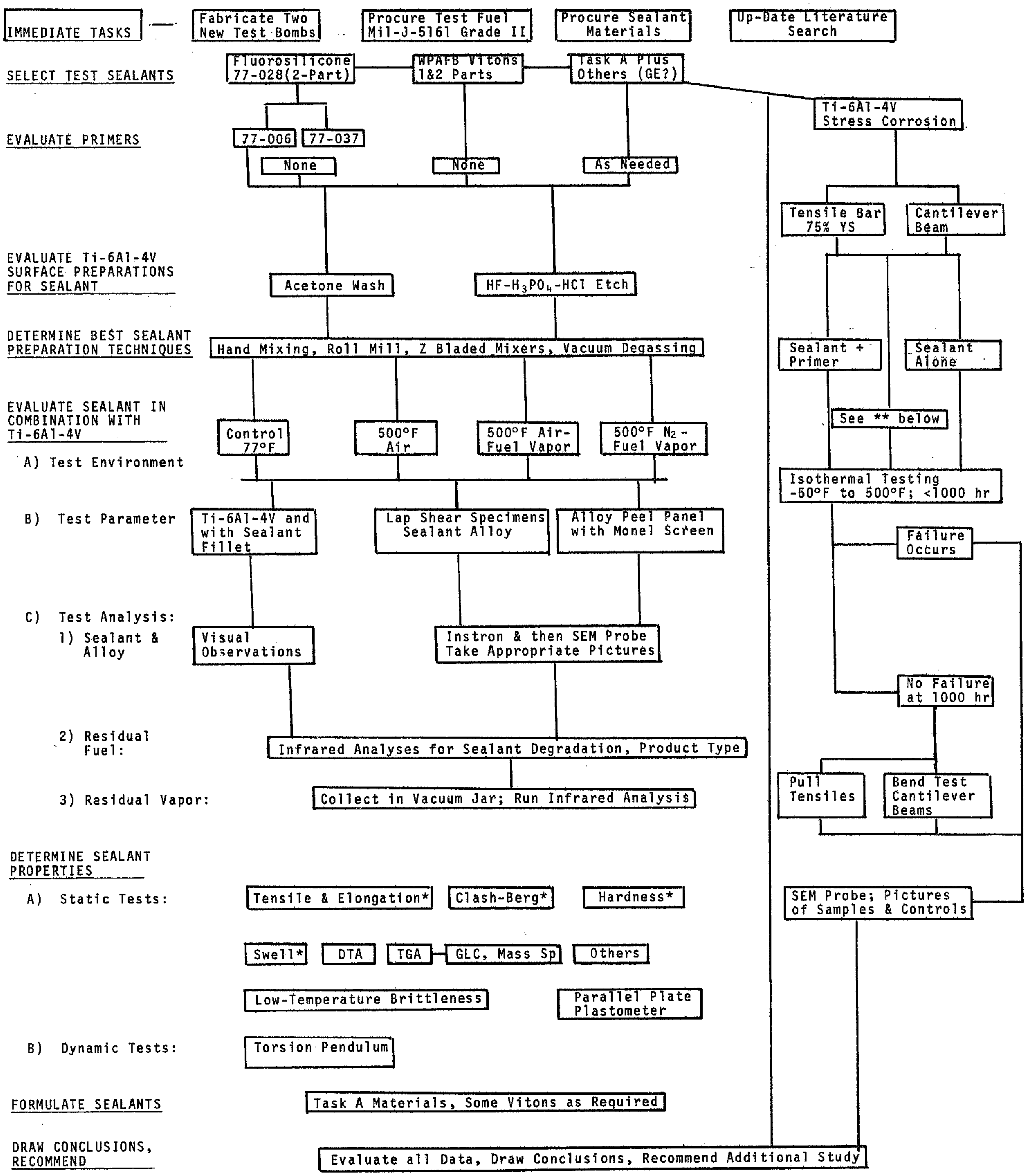
Contained exactly the same ingredients as found in the Viton sealant fuel-air vapor, with unidentified components having absorption bands at 7.90, 8.45, and 8.65 micron wavelengths.

4. Fuel Vapors (Nitrogen Exposure):

The Q-112 sample has the same ingredients as found in the control, plus large amounts of CO, CO_2 and H_2O.

The Q-113 sample has the same ingredients as found in the control, plus a large amount of CO. There was no detectable CO_2 or H_2O. The same unidentified components as described above for the fuel-air sample were also present in this sample.

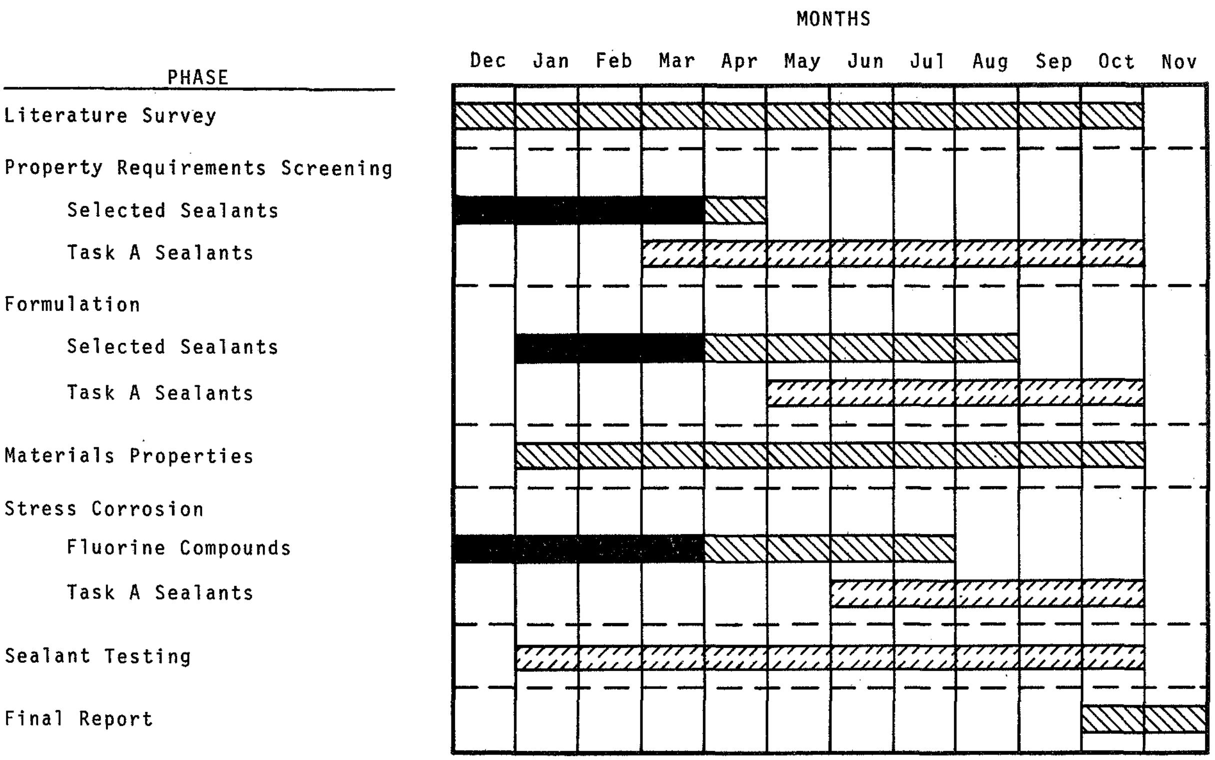
PROGRAM PLANNING PERT CHART



** Test non-corroding sealant system using HF acid etch treatment; acetone wash is standard

* Will be run before and after above mentioned environmental exposures

PROGRAM PLANNING CHART (Second Year - 1970)



MANPOWER

	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
Cumulative Hours (3800 projected)	83	249	381	606	910	1217						

Procurement

Study of Sealants Currently Available

Indicates Possible Period over which Task A Materials May Become Available

CONTRACT BUDGET
Monsanto Research Corp.
Dayton Laboratory

Job No. 5509

Samuel Steingiser
Project Mgr.

Date: 31 May 1970

HIGH TEMPERATURE FUEL TANK SEALANTS - TASK B
Title

NAS8-21399
Contract No.

Starting Date: 28 June 1968

End of Experimental Work: 30 Oct. 1970

Completion Date: 30 Nov. 1970

Duration: 29 months

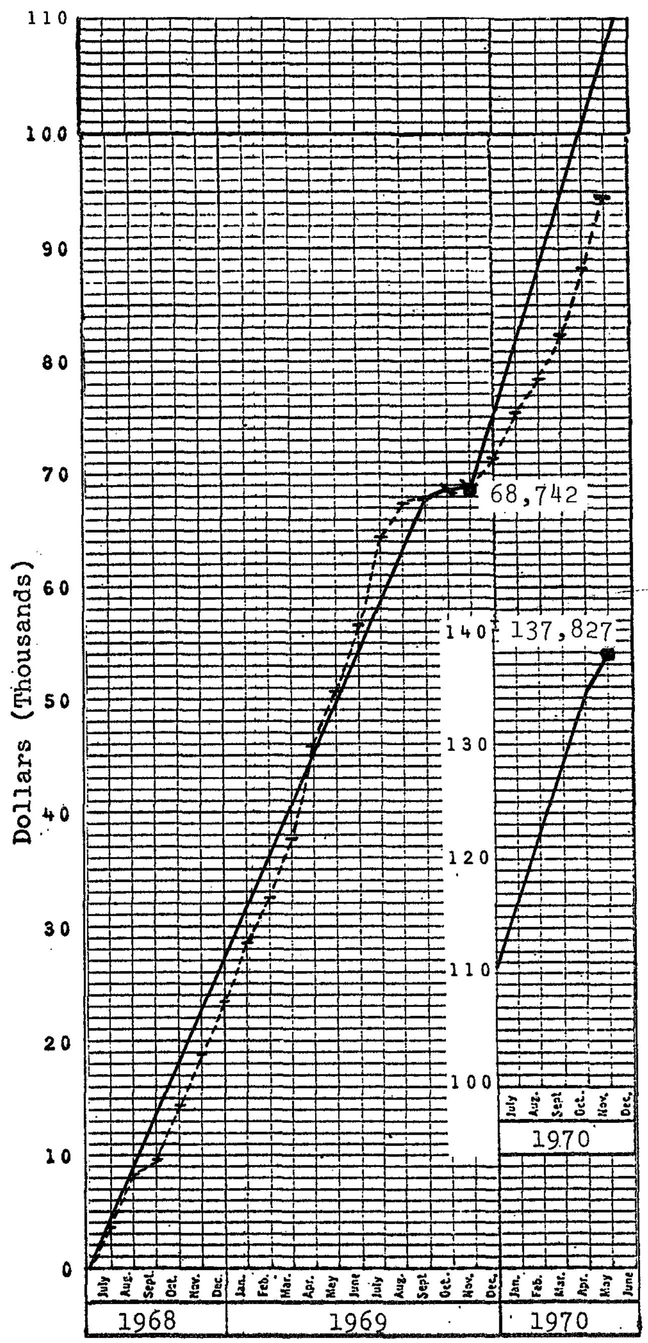
Contract Cost, Exclusive of Fee: $137,827

Cost for Final Report: $ 3,085

	Budget		Actual	
Date	Mo.	Year	Mo.	Year
7/68	4500	4,500	3520	3,520
8/68	4500	9,000	4583	8,103
9/68	4500	13,500	1652	9,755
10/68	4500	18,000	5454	14,117
11/68	4500	22,500	3071	18,967
12/68	4500	27,000	4403	23,370
1/69	4500	31,500	4781	28,677
2/69	4500	36,000	3813	32,490
3/69	4500	40,500	5194	37,684
4/69	4500	45,000	8241	45,925
5/69	4500	49,500	4709	50,634
6/69	4500	54,000	6012	56,646
7/69	4500	58,500	7547	64,193
8/69	4500	63,000	3237	67,430
9/69	4500	67,500	284	67,714
10/69	1000	68,500	935	68,649
11/69	242	68,742	235	68,884
12/69	6000	74,742	2477	71,361
1/70	6000	80,742	4138	75,499
2/70	6000	86,742	2729	78,228
3/70	6000	92,742	4055	82,283
4/70	6000	98,742	5830	88,113
5/70	6000	104,742	6341	94,454
6/70	6000	110,742		
7/70	6000	116,742		
8/70	6000	122,742		
9/70	6000	128,742		
10/70	6000	134,742		
11/70	3085	137,827		

Projected Expenditures ——— (Exclusive of Fee)

Actual Expenditures -----



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